

# PATENT SPECIFICATION (11)

1 439 469

1 439 469

- (21) Application No. 57744/73 (22) Filed 13 Dec 1973  
 (31) Convention Application No. 2261456 (32) Filed 15 Dec 1972 in  
 (33) Germany (DT)  
 (44) Complete Specification published 16 Jun 1976  
 (51) INT CL<sup>2</sup> GOIN 31/12  
 (52) Index at acceptance

G1B 12B3 12B5 13AX 16A 17X1  
 18D 18E 22L



## (54) "PROCESS FOR THE PYROLYTIC ANALYSIS OF LIQUIDS"

(71) We, BAYER AKTIENGESELLSCHAFT, 509 Leverkusen, Germany. A body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the pyrolytic analysis of liquids.

Pyrolytic analyses have recently been used for the analysis of sewage. Analyses of this kind are of considerable importance because the chemical and biological reactions which take place in treatment plants are governed to a very large extent by the composition of the sewage. One interesting parameter is for example the total carbon content of the sewage. To determine total carbon content, the hydrocarbon compounds present in a small sample of sewage are catalytically burnt in a furnace to form carbon dioxide. The carbon dioxide is quantitatively detected using a commercial CO<sub>2</sub> analyser (C.E. Van Hall, J. Safranko, V. A. Stenger: Rapid Combustion Method for the Determination of Organic Substances in Aqueous Solutions, Anal. Chem. 35 (1963) 3, 315/507; C. E. Van Hall, V.A. Stenger: An Instrumental Method for Rapid Determination of Carbonate and Total Carbon in Solutions, Anal. Chem. 39 (1967) 4, 503/507). A portable analyser which functions using this method is commercially available (Analyser for dissolved, organically combined carbon, model 915 of Messrs. Beckmann Instruments GmbH, 8 Munich).

An automatic instrument for the determination of organic carbon in water uses a capillary for introducing the liquid into the furnace (G. Axt: Ein Gerat zur kontinuierlichen Messung des organischen Kohlenstoffs in Trinkwasser- und Abwasserbereichen [an instrument for continuously measuring the organic carbon in drinking water and sewage] from Wasser 36 (1969) 328/339 und Haus der Technik-

Vortragsveroeffentlichungen, Essen).

It is also known that the total oxygen demand of a sewage sample can be determined by pyrolytic analysis. In this case, a small sample of sewage is injected into a combustion furnace through which carbon dioxide flows. Incompletely oxidised substances are oxidised by the carbon dioxide and form carbon monoxide which is determined in an analyser and represents a measure of total oxygen demand (V. A. Stenger, C. G. Van Hall: Rapid Method for Determination of Chemical Oxygen Demand, Anal. Chem. 39 (1967) 206/211; Precision Aqua Rator for Chemical Oxygen Demand, manufactured by Messrs. Precision Scientific Co., Chicago, USA. In another process, the decrease in oxygen during combustion of the sewage sample is measured (Total Oxygen Demand Analyser, model 225 of Messrs. Ionics Corporation, Watertown, Massachusetts, U.S.A.).

The object of the present invention is to improve the pyrolytic analysis of liquids in regard to reproducibility and accuracy. In conventional processes, the catalysts frequently show signs of poisoning in the combustion furnaces. At the relatively low temperatures applied, this results in incomplete combustion of the sample. Unfortunately, the result of measurement is rendered inaccurate and unreliable in this way. Accordingly, the purpose of the invention is to improve pyrolytic analysis in such a way that reliable and accurate routine measurements are possible. It is only in this way that pyrolytic analysis, hitherto carried out predominantly on a laboratory scale, can be used for the continuous monitoring of operations.

According to the invention there is provided a process for the pyrolytic analysis of liquids, wherein a sample of the liquid to be analysed is injected, together with a carrier gas comprising air, into a combustion furnace and passed repeatedly through the hottest zone of the furnace where the sample is burnt in the

absence of a catalyst at temperatures of from 1000 to 1200°C, and the combustion gases formed are delivered to an analyser.

The carrier gas preferably comprises air from which all the carbon compounds have been removed by pre-combustion and CO<sub>2</sub>-sorption.

The water vapour formed in the combustion chamber is with advantage removed in order to prevent condensation in the input and output pipes of the combustion furnace.

The process according to the invention is particularly suitable for determining the total carbon content of a liquid sample. For this purpose, the sample is completely burnt to form CO<sub>2</sub> and water and the quantity of CO<sub>2</sub> formed quantitatively determined in a CO<sub>2</sub>-analyser.

In addition to the total carbon content, total oxygen demand is an important parameter. Accordingly, in a further development of the invention, the decrease in free oxygen content of the carrier gas is determined during combustion of the sample to be analysed by comparative measurement of the free oxygen concentration in the carrier gas before and after the combustion process.

Determination of the total oxygen demand can be combined with determination of the total carbon content. In this case, both measurements are carried out simultaneously in one and the same sample. It is possible in this way to obtain two complementary measurements which are much more indicative, especially in the analysis of sewage.

It is particularly important to examine liquids for traces of mercury. It has been found that pyrolytic mercury analysis is much simpler than conventional wet chemical analysis. According to a further development of the invention, the pyrolytic analysis of liquids containing mercury is carried out by decomposing a mercury-containing sample in the combustion furnace to produce atomic mercury and by delivering the mercury vapour formed to a mercury analyser at temperatures above 100°C.

One apparatus suitable for this purpose comprises a combustion furnace having a liquid injection valve and a mercury absorption photometer connected to the outlet of the furnace. The combustion furnace advantageously consists of several tubes arranged one inside the other so that during combustion the injected sample passes repeatedly through the hottest zone of the furnace. In the case of sample liquids whose composition changes as a function of time, analysis has to be constantly repeated. In this case, the injection valve is with advantage installed in such a way that the liquid to be analysed flows constantly through it.

Water vapour should be prevented from condensing in the measuring cell of the absorption photometer. For this reason, the pipes connecting the combustion furnace to the absorption photometer and the measuring cell

are best heated to a temperature above 100°C, preferably to a temperature of 150°C. In a further embodiment, nozzles are arranged along the sills of the cell windows from which nozzles mercury-free rinsing air flows onto the windows or into the cell.

In an alternative embodiment, the heated connecting pipe is in the form of a capillary having an internal diameter of 1 to 4 mm and a length of 200 to 400 mm. In this case, the combustion gases formed during pyrolysis flow slowly into the measuring cell so that there is no need for cell windows, since there are no sudden pressure variations in the cell, so that gases from the atmosphere (possibly mercury containing) cannot enter the measuring cell and influence the absorption. If, on the other hand, the cell was not run at steady state conditions, air could be drawn into the cell by a sudden decrease in pressure, so that analysis would be falsified.

The advantages afforded by the invention are embodied in increased reproducibility and accuracy of measurement coupled with a greater degree of reliability. Complete combustion is always obtained by virtue of the particular flow path and the high temperature prevailing in the combustion furnace. With minor modifications in terms of apparatus, the process according to the invention can readily be used for determining other components as well (for example analysis of heavy metals). It is particularly suitable for the continuous monitoring of sewage streams before they flow into treatment plants.

Embodiments of the invention are described by way of example in the following with reference to the accompanying drawings, wherein:

Figure 1 is a block diagram for the pyrolytic analysis of the total carbon content of a sewage sample.

Figure 2 shows the structure of the combustion furnace.

Figure 3 is a block diagram for simultaneous determination of the total carbon content and total oxygen demand of a sewage sample.

Figure 4 is a block diagram for the pyrolytic analysis of mercury.

Figure 5 shows part of the measuring cell in a mercury absorption photometer.

The most important part of the analyser in Figure 1 is the combustion furnace 1 with the injection valve 2. It consists of a quartz tube 3 which is electrically heated to 1000 to 1200°C. The temperature is kept constant by means of a control circuit. The structure of the furnace 1 is shown in Figure 2. The carrier gas charged with the injected sample flows through two tubes 5 and 6 arranged one inside the other and, in this way, flows repeatedly through the hottest zone of the furnace. The carrier gas enters the innermost tube at the inlet opening 7. The combustion furnace 1 contains an additional combustion chamber 8 for precom-

bustion of the carrier gas. The combustion gases are delivered to the analyser through the outlet opening 9.

Atmospheric air is used as the carrier gas. The gaseous carbon dioxide present in it and any hydrocarbon compounds (oil mist etc.) present are completely removed except for a small constant residue in a separate air preparation unit. The air preparation unit consists of zeolite adsorbers 10 and 11, the pre-combustion chamber 8 arranged between these two adsorbers, a pressure controller 12 with an adjusting valve and a flow meter 13 for adjusting a constant carrier gas pressure. A carrier gas stream of about 10 litres per hour to 30 litres per hour is adjusted by means of the pressure controller 12 and the throughflow meter 13. A non-return valve 14 prevents water vapour from entering the air preparation unit.

The metering valve 2 injects approximately 20 micro-litres of sewage into the innermost tube of the combustion furnace 1. The sewage sample can also be manually injected by means of a microlite injector. The hydrocarbon compounds present in the sewage burn immediately at 1000 to 1200°C to form carbon dioxide. In contrast to conventional furnaces, the combustion furnace 1 works in the absence of a catalyst. Investigations have shown that the effectiveness of conventional catalysts is seriously impaired by the sulphur compounds normally present, and gradually drop out. In view of the high temperatures referred to, all the hydrocarbon compounds are completely burnt to form carbon dioxide. Any further increase in temperature beyond 1200°C does not increase the yield of CO<sub>2</sub>.

The CO<sub>2</sub> formed flows through the outlet 9 to the analysis unit. The CO<sub>2</sub>-analyser is preceded by a washing bottle 15 filled with calcium chloride granulate which absorbs the water vapour formed in the combustion chamber. Since the carrier gas is extremely dry, some of the water vapour absorbed is slowly given off again between two injections of sewage. In any event, the dew point of the combustion gases should be lowered to such an extent that condensation of the water vapour in the analysis unit is avoided.

A dust filter 16 protects the following carbon dioxide analyser 17 against contamination. The recording unit 18 records the individual carbon dioxide concentrations of the injected samples. Both the integrated total carbon dioxide concentration and also the maximum carbon dioxide concentration can serve as a measure of the carbon content in the water. A suitable CO<sub>2</sub> analyser is commercially available (Uras 2 manufactured by Messrs. Hartmann & Braun AG, Frankfurt, or Unor 2 manufactured by Messrs. Maihak AG, Hamburg) (The word "Unor" is a Trade Mark).

The shortest possible interval between two successive analyses is approximately 2 minutes. This dead time is due to the need to flush

the combustion furnace after each injection. The carbon dioxide which is formed in the combustion furnace and which has flowed into the analysis section 15, 16, 17, 18 is only gradually degraded by the carrier gas.

The combined determination of total carbon content and total oxygen demand is diagrammatically illustrated in Figure 3. The air preparation unit is used to remove carbon fractions from the air delivered into the pre-combustion chamber 8 and the following zeolite adsorber 11.

The total oxygen demand is determined by measuring the oxygen content of the carrier air before and after combustions. A high-temperature zirconium oxide measuring cell 19 is used for measuring the oxygen. A component stream of the carrier air is branched off before the inlet into the combustion furnace 1 and is used as a comparison gas stream. The oxygen content of this component stream is the reference point for oxygen measurement after combustion. In this way, fluctuations in the oxygen concentration of the carrier air have only a limited effect upon measurement of the total oxygen demand. The recorder 18 continuously records the total carbon content and total oxygen demand of the sewage alongside one another.

Determination of the total mercury content of a sewage sample is illustrated in Figure 4 as another example of an application of the invention. The air is drawn in by a pump 22 through a dust filter 20 and a mercury filter 21 (silver wool), and delivered under pressure into the combustion furnace 1 through an adjusting valve 23a, a flow meter 13 and a non-return valve 14. The gas throughput amounts to approximately 30 litres per hour. Combustion again takes place at around 1000 to 1200°C. As already described, the combustion chamber consists of several tubes arranged one inside the other. The sample liquid can be injected into the combustion furnace either manually by means of a microlitre injector or automatically by means of the injection valve 2.

The carrier gas with the evaporated and pyrolysed liquid sample flows through as short a heated tube 24 as possible directly into the heated measuring cell 25 of a mercury adsorption photometer 26 of the Okometer B-type manufactured by Messrs. Withof GmbH, Kassel. The main components of this instrument are the measuring cell 25, the comparison cell 27, the light source 28 and the receiver 29.

The temperature prevailing in the measuring cell 25 and connecting line 24 is around 150°C. Water vapour is formed at temperatures below 100°C, accumulating in the pipes and in the measuring cell 25. However, water vapour mists and deposits on the windows 30 of the measuring cell would seriously interfere with measurement of the mercury. In order to prevent coating of the cell windows 30, annular nozzles 31 (see Figure 5) are arranged along both

windows. These nozzles are connected to the mercury-free carrier air through the pipes 32 and the adjusting valves 23b and 23c.

The annular nozzle 31 consists of a hollow ring with 7 jets directed obliquely inwards or outwards. The rinsing air flows through these jets into the measuring cell 25 at a rate of approximately 15 litres per hour. The flow rate is adjusted by means of the adjusting valves 23b, 23c, and controlled by the flow meters 33. The pipes 32 through which the rinsing air is delivered are also heated to prevent the measuring cell from cooling. For reasons of heating technology, the rinsing air pipes 32 are arranged along the measuring cell 25 and are heated together with it.

The combustion gas and the rinsing gas are drawn off from the measuring cell 25 by means of a pump 34. A flow meter 35 and an adjusting valve 36 are used to adjust the flow rate of approximately 60 litres per hour.

The measuring cell 25 can also be made without windows providing the connecting line 24 is in the form of a capillary and the jets of the annular nozzle 31 are directed inwards. In this case, the combustion gases formed during pyrolysis do not flow suddenly into the measuring cell 25. Since the throughput of the suction pump 34 is in equilibrium with the flow rate of the gases flowing in (the carrier gas, combustion gas and rinsing air), no gases are able to enter the space between the measuring cell 25 and the emitter 28 and receiver 29.

The recorder 37 connected to the receiver 29 records the mercury concentration of each individual sewage sample in the form of a deflection. Determination of the mercury content of sewage is of considerable importance on account of its high toxicity and its marked influence upon the biological clarification mechanism.

Co-pending application No. 57979/73 (Serial No. 1439470) relates to an apparatus for the pyrolytic analysis of liquids, comprising a combustion furnace comprising a plurality of combustion chambers arranged one inside the other in such a manner that a gas stream passed therethrough is repeatedly deflected through 180° and is passed repeatedly through the hottest zone of the furnace, an injection valve adapted to be continuously fed with the liquid to be analysed and to inject the liquid into the furnace and an analyser connected to the outlet of the combustion furnace.

#### WHAT WE CLAIM IS:-

1. A process for the pyrolytic analysis of liquids, wherein a sample of the liquid to be analysed is injected, together with a carrier gas comprising air, into a combustion furnace and passed repeatedly through the hottest zone of

the furnace where the sample is burnt in the absence of a catalyst at temperatures of from 1000 to 1200°C, and the combustion gases formed are delivered to an analyser.

2. A process as claimed in claim 1, wherein the carrier gas comprises air from which all the carbon compounds have been removed by pre-combustion and CO<sub>2</sub>-sorption.

3. A process as claimed in claim 1 or 2, wherein water vapour formed in the combustion furnace is removed before the combustion gases are delivered to the analyser.

4. A process as claimed in any of claims 1 to 3, wherein in order to determine its total carbon content, a carbon-containing sample is completely burnt to form carbon dioxide and water and the quantity of carbon dioxide formed is quantitatively determined in a carbon dioxide analyser.

5. A process as claimed in any of claims 1 to 4, wherein the decrease in free oxygen content of the carrier gas during combustion of the sample is determined by a comparison measurement of the concentration of free oxygen in the carrier gas before and after combustion.

6. A process as claimed in either of claims 4 and 5, wherein determination of the carbon content of the sample and determination of the decrease in free oxygen content of the carrier gas are carried out simultaneously.

7. A process as claimed in claim 1, wherein a mercury-containing liquid sample is decomposed to form atomic mercury in the combustion furnace and the mercury vapour formed is delivered to a mercury analyser at temperatures above 100°C.

8. An apparatus when used for carrying out the process as claimed in claim 7, comprising a combustion furnace having a liquid injection valve and a mercury absorption photometer connected to the outlet of the furnace.

9. An apparatus as claimed in claim 8, wherein a connecting line from the combustion furnace to the mercury absorption photometer and its measuring cell is heated to a temperature above 100°C and preferably to a temperature of 150°C.

10. An apparatus as claimed in Claim 9, wherein the measuring cell comprises windows and annular nozzles are arranged along the sills of the cell windows for blowing dry mercury-free rinsing air onto the windows.

11. An apparatus as claimed in claim 9, wherein the heated connecting line is in the form of a capillary with an internal diameter of 1 to 4 mm and a length of 200 to 400 mm and the measuring cell is windowless and comprising annular nozzles arranged one at each end of the cell and directed into the body of the cell.

---

A. POOLE & CO.,  
Chartered Patent Agents,  
54 New Cavendish Street,  
LONDON W1M 8HP.

---

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1976.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

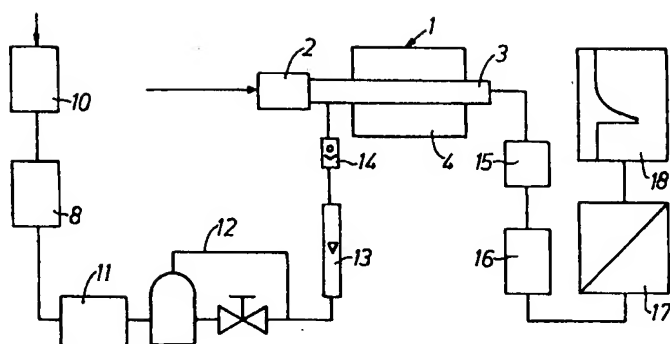


FIG. 1

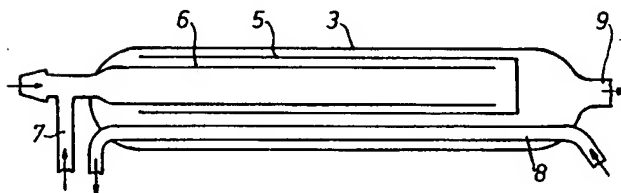


FIG. 2

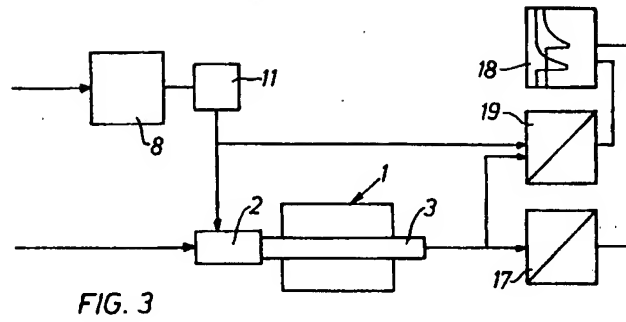


FIG. 3

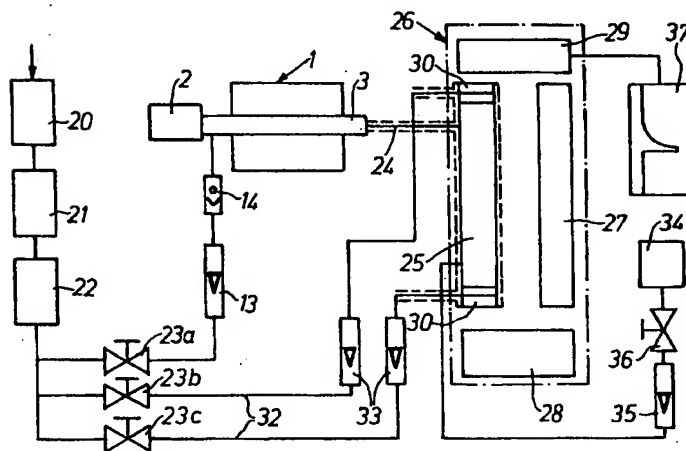


FIG. 4

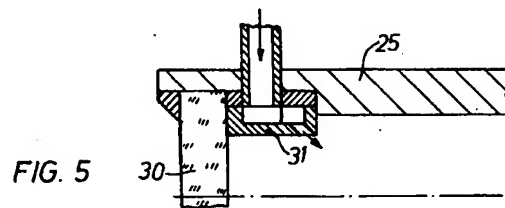


FIG. 5